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Study on Specific Heat of Water Adsorbed in Zeolite Using DSC

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Abstract In this study, the specific heat of water included in an adsorbent was analyzed by a differential scanning calorimeter in the temperature range from −50 °C to 50 °C. Zeolites with pore sizes of 3 Å and 9 Å were employed as adsorbents, and the measurement was performed with various water mass fractions in zeolites. In this article, the water was defined as being composed of adsorbed water and free water that is not adsorbed in zeolite. As a result, the specific heat of the dry zeolite increased with temperature. The specific heat of the adsorbed water was measured by a special experimental procedure to establish the experimental accuracy. It was found that the specific heat of the adsorbed water had values in the range from (3 to 5) $J \cdot g^{-1} \cdot K^{-1}$.

Keywords Adsorbed water · Differential scanning calorimeter (DSC) · Specific heat · Zeolite

1 Introduction

The freezing phenomenon of a porous layer including permeated water is an important problem in food freezing. The underground laying of an LNG reserve tank and the maintenance for a pipe line of LNG in cold regions are the examples of numerous investigations [1–4] involving the solidification and melting process of porous layers with permeated water. However, few investigations have been performed on the

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thermal properties of water included in particles with a microstructure. The authors have carried out an experimental analysis [5,6] for the latent heat and for the effective thermal conductivity of a zeolite packed bed for the purpose of considering the thermal phenomena associated with the solidification and melting of water in a microstructure.

In this article, the specific heat of adsorbed water in an adsorbent was analyzed by a differential scanning calorimeter (DSC) in the temperature range from −50 °C to 50 °C. The experimental values were compared with the specific heats of normal water or ice and analyzed/discussed by associating the results with the state of water.

2 Specimens

The adsorbents employed in this study are the synthetic zeolites A3 and F9, and molecular sieve 13X. The physical properties are shown in Table 1, in which, the heat of adsorption is the heat generated by adsorbing 1 g of water, which are the measured values from the calorimeter employing the mixture method as shown in Fig. 1, by mixing the dry adsorbent and water. A micropore as the adsorption site of the zeolite has the size of several times that of the water molecule, and it is a uniform size.

Table 1 Physical properties of zeolite

Specimen	Pore size (Å)	Maximum ratio of adsorbed water (mass %)	Specific heat ($kJ \cdot kg^{-1} \cdot K^{-1}$)	Heat of adsorption ($kJ \cdot kg^{-1}$)
Zeolite A3	3	20	0.87	1183
Zeolite F9	9	26	0.82	1019
Molcular sieve 13X	9	36	0.91	1132

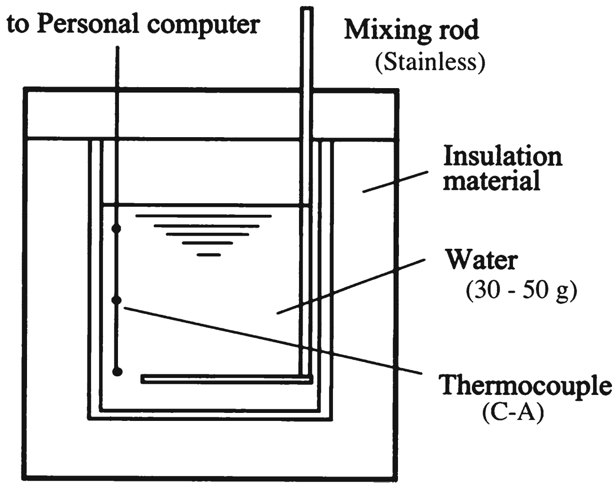


Fig. 1 Schematic diagram of calorimeter for mixing method

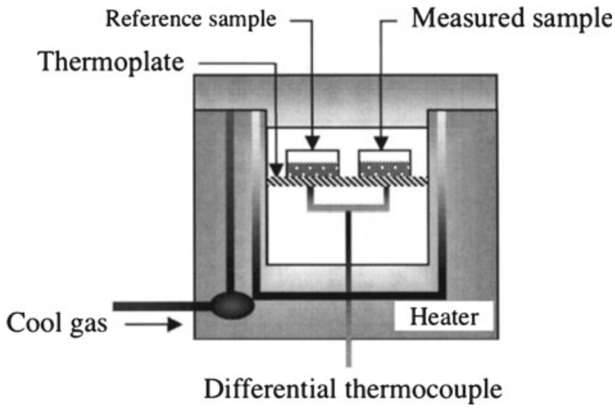


Fig. 2 Outline of DSC

3 Experimental Apparatus and Procedure

Figure 2 is a schematic of the DSC employed in this experiment for measuring the specific heat. In this apparatus, the measured signal is the difference of the temperature response, DSC curve, between the reference material and the sample when a constant and uniform heat flux is applied; thus, the DSC curves indicated in Fig. 3 are needed for determining the specific heat of the sample. The specific heat is given by the following equation:

$$c_p = c_{\mathrm{st}}\,(m_{\mathrm{st}} H_{\mathrm{sa}} / m_{\mathrm{sa}} H_{\mathrm{st}}) \tag{1}$$

where $c_p, m,$ and H are the specific heat, mass, and the shift of baseline, respectively, and subscripts "st" and "sa" correspond to the reference material and sample, respectively.

For verifying the precision of the measuring method, the specific heat of ice was measured using α-alumina as a reference material. The result is shown in Fig. 4, in which, the solid line is the reference value [7]. The measurements are performed for temperature rate increases of $4\,^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$ and $5\,^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$. It is found that the measured specific heats agree with the reference value. Consequently, in this study $5\,^{\circ}\mathrm{C} \cdot \mathrm{min}^{-1}$ is employed as the heating rate.

4 Results and Discussion

For the purpose of measurements for the specific heat of adsorbed water, two pieces of dry zeolite with the same mass are prepared; the mass measurement is carried out by an electronic balance with a precision of 0.01 mg, and one of these pieces of dry zeolite is employed as the reference material and the water is adsorbed in the other zeolite sample up to a given mass fraction. Thus, the specific heat of the adsorbed water is determined directly using Eq. 1 as shown in Fig. 3.

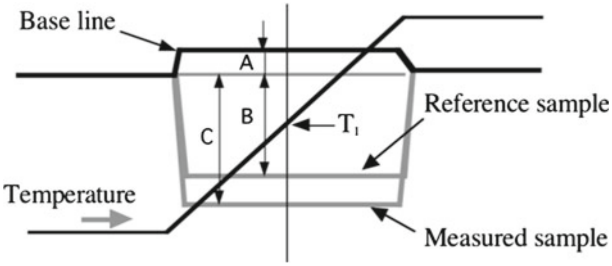
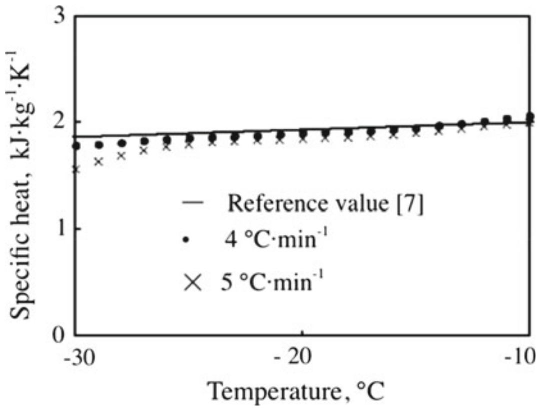


Fig. 3 Principle of the measurement of specific heat

Fig. 4 Relation between specific heat of ice and temperature



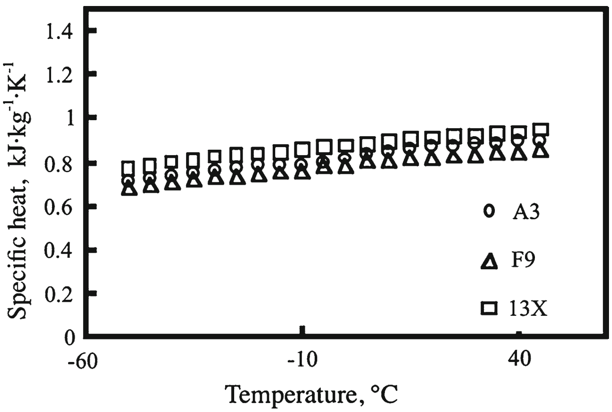


Fig. 5 Relation between specific heat of dry zeolite and temperature

Figure 5 shows the relationship between the specific heat and temperature for dry zeolite from −50 °C to 50 °C. Since A3 and F9 have almost the same composition of the component and 13X has a little different composition from these, the specific heats of A3 and F9 are almost equal and 13X has larger values of the specific heat over the complete temperature range.

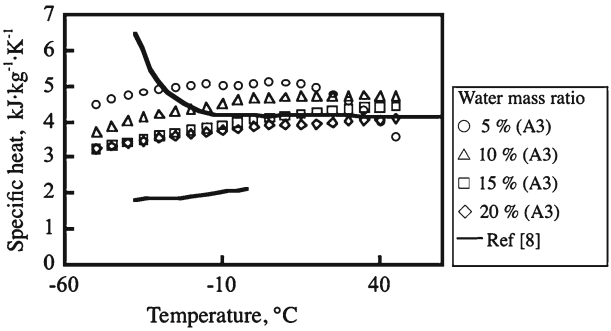


Fig. 6 Relation between specific heat of absorbed water and temperature (A3)

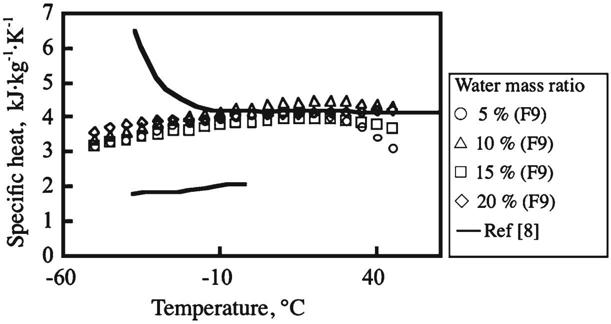


Fig. 7 Relation between specific heat of absorbed water and temperature (F9)

Figure 6 shows the relation between the specific heat for adsorbed water in zeolite A3. In this figure, the solid line is the reference values of ice [7] and of supercooled water [8]. The specific heat of the adsorbed water is about (3 to 5) $J \cdot g^{-1} \cdot K^{-1}$. At temperatures lower than $-10\,°C$, these values are lower than that of supercooled water and higher than that of ice. This is understood in that the adsorbed water does not go through a phase change [5] and the water existing in the microstructure is the size of a few nanometers, such as glassy water, ice, etc., and has different characteristics from that of a water cluster [9,10]. It is found that the specific heats for the low adsorption ratios are relatively large compared to other ratios, and near room temperature, the specific heat shows a decrease with an increase in temperature. These phenomena may be caused by the fact that the micropore size of A3 is 3 Å which is on the same scale as a water molecule, and the physical characteristics of adsorbed water are different from the nature of a water cluster.

Figures 7 and 8 show the results for the specific heats of adsorbed water in zeolites F9 and 13X, respectively. From these figures it is found that the specific heats increase gradually with increasing temperature and that the values are in the range of (3 to 4.5) $J \cdot g^{-1} \cdot K^{-1}$. It is found that the adsorbed water in the relative large adsorption site is also in the state of glassy ice. In this case, the specific heat of 5 % adsorbed water is close to others that are different from the case of A3. This fact may suggest that the

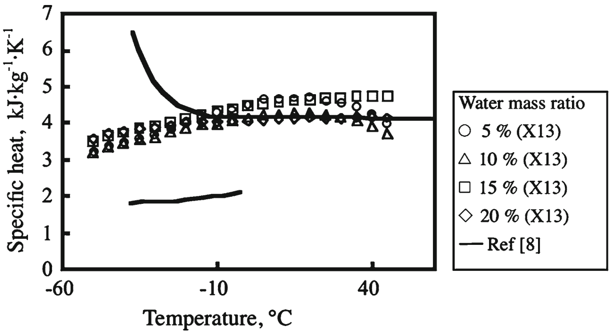


Fig. 8 Relation between specific heat of absorbed water and temperature (13X)

adsorbed water in the adsorption site with the relative large size has few characteristics of a water cluster.

5 Conclusion

The specific heat of adsorbed water in an adsorbent was analyzed by DSC in the temperature range from −50 °C to 50 °C. The following results were obtained:

1. The specific heat of adsorbed water was about (3 to 5) $J \cdot g^{-1} \cdot K^{-1}$.
2. The specific heat of adsorbed water was lower than that for supercooled water in the temperature range below −10 °C and it showed the physical characteristics of such as glassy ice.
3. The adsorbed water has no phase change, and in the case of a small pore size, the characteristics are different from those of a water cluster.

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